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**EVALUATION OF SYSTEMATIC AND RANDOM ERROR
IN THE MEASUREMENT OF EQUILIBRIUM SOLUBILITY AND
DIFFUSION COEFFICIENT FOR LIQUIDS
IN POLYMERS**

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PREFACE

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**EVALUATION OF SYSTEMATIC AND RANDOM ERROR
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1. INTRODUCTION

The investigation's main objective was to measure the error contributed by several critical experimental procedures. The methodology evaluation supported the development of standardized experiments to measure the degree of interaction between a polymer material and a toxic liquid. The measurement goal was to yield the equilibrium solubility (total sorption or swelling) equivalent determined in ASTM D471, ASTM D543, and the ARL immersion test. The goal also was to include the determination of fraction of polymer additives extracted, comparable to the equilibrium solubility equivalent described in ASTM D471. An additional objective was to provide an option to these methods that minimized toxic liquid volume and experimental manipulations of toxic specimens. A further objective was to develop a method that would yield the contaminant desorption rate and determine the diffusion coefficient. The technique was specifically developed to measure high data densities over the entire desorption curve and allow computation to the first derivative to obtain access to diffusion coefficient estimates in the low concentration regime. Finally, the permeation was to be calculated from the measurement of solubility and diffusion. The solubility and diffusivity values were to provide input to permeation models for droplet and film geometries.

In any area of research, the standardization of experimental methodology contributes to the acceptance of the method because the experiment can be repeated to generate comparable data. When the material under study is a polymer, the importance of methodology standardization increases because subsequent lots of the same polymer are rarely identical.

2. EXPERIMENTATION

2.1 Instrumentation.

A horizontal microbalance was used because this configuration provided an environmental wind tunnel geometry (TA Model, 951 TGA). The nominally dime-sized specimen was suspended from a custom-wire holder that was designed to suspend a 10-60 mil thick circular sheet specimen. The various wire holders accommodated specimens that might swell to some variable new diameter up to ca. 0.70 in. A custom Model PDP 11/24 (Digital Equipment Corp, Maynard, MA) data acquisition/control/computational computer¹ interfaced to the thermogravimetric analyzer (TGA) supplemented the Model 990 Controller. The differential amplifiers have numerous offset and scaling functions. These scaling functions were used, along with those built in to the TGA

electronics, to assist in various taring strategies. Any commercial TGA or recording microbalance system could be adapted to this experiment.

2.2 Materials and Procedures.

The materials employed were those from a standard set of elastomers developed and characterized at the U. S. Army Research Laboratory (ARL).² The abbreviated names and compositions of the elastomers are listed in Table 1. A series of proprietary elastomers was studied from McDonnell Douglas Corporation (Los Angeles, CA) consisting of custom polymerized silicone, urethane based polymers, and a Neoprene sample from ASTM.^{3,4} Additionally, immersion sorption rates with DIMP and DCP have been determined at ARL.⁵ The ARL immersion test is a non-standardized test that is similar to ASTM D471 except that the procedure does not determine and correct for fraction extracted as called for in ASTM D471. The chemical names and liquid codes for these and other model liquids are listed in Table 2.

2.3 Method Diagram.

A diagram of mass-loss, as a function of time for concurrent liquid sorption, is shown in the Figure. The additive extraction, followed by a desorption measurement of diffusion coefficient, is also shown. Mass is shown on the y-axis versus time on the x-axis. The time axis is separated into three phases.

Phase 1 is the sorption-with-extraction phase during which additives are being extracted at the same time that liquid is being sorbed into the elastomer. Phase 2 is the desorption phase in which the fully sorbed sample is placed on a microbalance and the weight loss due to liquid desorption versus time is recorded. Data obtained in this phase are used to calculate the diffusion coefficient. Phase 3 is the accelerated desorption phase and might be necessary to drive the diffusion of residual sorbed liquid contaminant to equilibrium in a reasonable time. This is necessary to obtain a more accurate measurement of the final sample weight to calculate the fraction extracted.

2.4 Fraction of Polymer Additive Extracted.

Fraction extracted is defined here as the sum of all of the mobile additives in a polymeric material that are susceptible to extraction by the test liquid. With respect to fraction extracted, ASTM D471, Section 13.2, directs the user "at the end of the required immersion period to remove the test specimens from the test tube and dry to a constant mass at a temperature of approximately 40 °C and an absolute pressure below 20kPa (150 mm Hg)." For the development of this method, the temperature of the TGA furnace was raised from 30 to 40 °C when the display of weight versus time for the experiment showed that the sample had apparently reached equilibrium at the 30 °C setting. The furnace was maintained at the elevated temperature of 40 °C until the

sample weight had again apparently reached its equilibrium value. Note that the TGA method can perform the ASTM correction for fraction extraction without further handling of the hazardous specimen.

3. RESULTS

3.1 Methodology Development.

The ASTM D471 method dealing with sorption/desorption of liquids in elastomers is quite general. A more specific subset of these procedures was developed to minimize the volume and minimize handling of hazardous specimens/solvents. Several critical aspects of the methodology were quantified with respect to systematic error, precision, and accuracy. Procedural errors quantified include the effect of blotting versus washing contaminant from specimens and the effect of desorption/evaporation loss during the transfer/weighing steps.

The overall precision was determined with three polymer/liquid systems with three to four repetitions each. The overall accuracy was estimated by comparing these values to concurrent determinations, using ASTM D471 with a macrobalance as the reference method.

3.2 Comparison of Systematic Error Due to Blotting Versus Washing.

The ASTM methods adapted to TGA instrumentation based methods required quantifying any systematic errors added by use of toxic chemicals and the TGA procedures. According to ASTM D471, Section 9.2, the user is directed to "dip the specimens quickly into acetone, blot lightly with filter paper free of lint and foreign material,..." It was decided to separate Section 9.2 into two components and compare blotting versus washing (dipping). This comparison was structured to demonstrate the relative abilities of these two contaminant removal procedures to remove all excess liquid surface contaminant from the sample. Specimen manipulation time was minimized to avoid desorption loss prior to loading the sample onto the microbalance. The test was performed as follows.

All specimens were cut using a cork bore of ca. 0.5 in., cleaned with warm oil-free soapy water (Ivory soap), dried with lint-free wipes, measured with a micrometer, and then weighed using the macrobalance. The washing was performed using gloves, which had been cleaned with warm oil-free soapy water. Stainless steel tweezers were used to handle the dried specimens.

The specimens were dipped in dimethyl methyl phosphonate (DMMP) and either blotted with wipes or washed with wash solvent, followed by re-weighing using the macrobalance.

Replicate experiments were performed using the BUTYL and Neoprene specimens. For the washing test, a non-solvent with a high vapor pressure and relatively different polarity was chosen for each elastomer type (methanol for BUTYL and pentane for Neoprene).

Table 3 presents a comparison of the blotting and washing procedures for removing the surface contaminant DMMP from elastomer specimens of ARL BUTYL and ASTM Neoprene. Columns 1 through 3 list the elastomer name, procedure used, and the wash solvent, where appropriate. Columns 4 and 5 list the initial weight and the final weight after the removal of the contaminant from the surface of the elastomer sample. The observed changes in weight are contained in columns 6 through 8. Column 6 lists the actual weight change, column 7 lists the actual weight change as a percentage of the initial sample weight, and column 8 lists the mean value for the percentages for each of the four unique elastomer/procedure/wash solvent combinations studied.

Results showed no significant difference between the two procedures. On the average, the blotting took about 15 sec/sample and the washing about 30 sec/sample. Therefore, for liquids with high vapor pressure and low sorption, the more rapid blotting procedure can be marginally recommended for removing excess liquid surface contaminant while minimizing time for desorption/evaporation.

3.3 Systematic Error Due to Desorption During Specimen Transfer.

After blotting/washing the sample, it takes approximately 42 sec to load the sample onto the microbalance, close the balance assembly, and allow the balance to stabilize at the maximum weight of the sample. The time interval is very crucial to the relative error when the sample has a low equilibrium solubility (ca. 5-10%), and the liquid has a high vapor pressure. The BUTYL/PCE and Neoprene/PCE elastomer/liquid combinations shown in Table 4 fall into the high volatility and solubility categories. The percentage error in the equilibrium solubility caused by this 42 sec delay is approximately -0.5%. However, to track this initial desorption time, one can obtain an accurate value for equilibrium solubility by starting the TGA timing function after blotting/washing the sample. Then, upon completion of the desorption experiment, one can extrapolate back to zero time to obtain the maximum weight.

3.4 Precision and Accuracy.

Data for the precision and accuracy of the overall method are shown in Tables 4a, 4b, and 4c. Table 4a contains data for equilibrium solubility (EqS), Table 4b contains data for diffusion coefficient (DC), and Table 4c contains data for fraction extracted (Ext). In all three tables, column 1 contains the elastomer, solvent, and balance combination studied, and column 2 contains the number of repetitions (Reps). Column 3 contains the

mean value for either EqS, DC, or Ext as specifically stated in each table. Column 4 contains the 95% confidence interval value for either EqS, DC, or Ext as specifically stated in each table. In addition, the accuracy of the EqS measurements of the TGA microbalance relative to the macrobalance is shown for each elastomer/solvent pair. The same specimens were used for the TGA and ASTM D471 macrobalance measurements for each unique elastomer/solvent pair, using the following procedure.

The ASTM D471 method was employed to allow prepared specimens to reach equilibrium in the contaminant. The specimens were then blotted dry and reweighed by macrobalance. The specimens were then replaced in their contaminant solutions, allowed to retain equilibrium, and desorbed on the microbalance. Equilibrium solubilities and percent extractables were calculated for the macro and microbalances. The equilibrium solubilities ranged from about 40 to 303%. Results showed no significant difference between macrobalance (ASTM D471) and microbalance data. Therefore, the microbalance method is preferred because it has the advantage of generating data to calculate diffusion coefficients.

4. DISCUSSION

The experimental results indicate that the method is suitable for measuring the difference in equilibrium solubility and diffusion coefficient among various polymer-liquid pairs. However, one must still be cautious in making comparisons between different materials because of differences in crosslink density and filler content. Scaling and normalizing each material sample with a reference solvent of near maximal sorption would improve the comparative ranking. Normalizing for filler content would further improve comparisons. Comparative rankings of materials, based on sorption, will erroneously rate a more highly crosslinked material more favorably relative to a less crosslinked material. The more highly crosslinked material may interact and sorb more strongly at the equivalent lower crosslink density.

5. CONCLUSIONS

The ASTM D471 and D543 methods modified for use with TGA instrumentation were determined to have good precision. This standard method of good precision allows important comparisons and rankings. Several liquids in a single material composition or several materials with a different liquid can be compared and ranked.

The systematic error due to volatilization during transfer is correctable to ca. 0%. Uncorrected systematic error is higher for a volatile liquid. However, for PCE (BP 121 °C), the error is only -0.5%.

The random error, defined by the 95% confidence interval as a percentage of the mean value, is as follows:

- Equilibrium Solubility $\pm 1.7-3.5\%$
 - Diffusion Coefficient $\pm 2\%$ for liquids with a boiling point (BP) $\geq 208^\circ\text{C}$
 $\pm 7-17\%$ for a liquid with a BP of 121°C
- (nominal Fickian)

The accuracy, defined by the difference in microbalance and macrobalance data as a percentage of macrobalance data, is $+ 1.2\%$ to $+ 2.8\%$.

FIGURE. DIAGRAM OF MASS-LOSS AS A FUNCTION OF TIME FOR CONCURRENT LIQUID SORPTION WITH ADDITIVE EXTRACTION FOLLOWED BY DESORPTION MEASUREMENT OF DIFFUSION COEFFICIENT

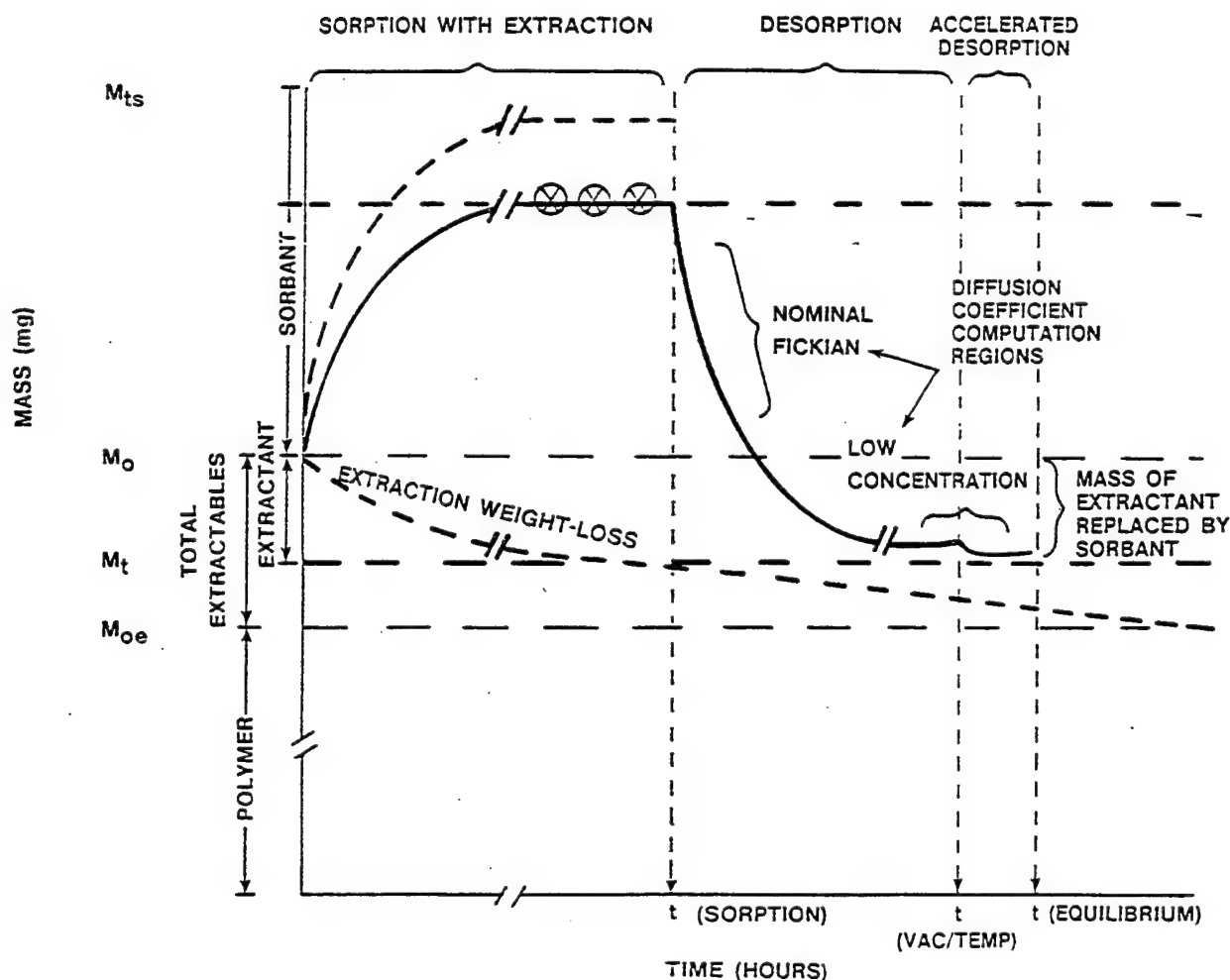


Table 1. Abbreviated Names and Polymer Compositions for the Series 2 Elastomers

Abbreviated Names	Polymer Compositions
BUTYL	poly (isobutylene/isoprene)
NEOPRENE	polychloroprene

Table 2. Liquid Codes and Chemical Names for Liquids Used to Interactions with Elastomeric Materials

Liquid Codes	Chemical Names
DMMP	dimethyl methylphosphonate
CEESS	2-chloroethyl ethyldisulfide
PCE	perchloroethylene, tetrachloroethylene

Table 3. Comparison of Blotting and Washing Procedures for Removing Surface Contaminant Dimethyl Methylphosphonate (DMMP) from Elastomer Samples of Butyl and ASTM Neoprene

Elastomer Procedure		Wash Solvent	Weight (mg)		Change		
			Init.	Final	Wt	%	Net, %
BUTYL	Blotting	NA	50.9	50.8	-0.1	-0.20	
BUTYL	Blotting	NA	51.7	51.6	-0.1	-0.19	-0.20
BUTYL	Blotting	NA	51.8	51.7	-0.1	-0.19	
BUTYL	Blotting	NA	51.1	51.0	-0.1	-0.20	
Neoprene	Blotting	NA	84.0	84.0	0.0	0.0	
Neoprene	Blotting	NA	85.2	85.3	+0.1	+0.12	+0.09
Neoprene	Blotting	NA	84.8	84.9	+0.1	+0.12	
Neoprene	Blotting	NA	82.0	82.1	+0.1	+0.12	
BUTYL	Washing	Methanol	50.8	50.6	-0.2	-0.39	
BUTYL	Washing	Methanol	52.1	51.9	-0.2	-0.38	-0.34
BUTYL	Washing	Methanol	52.1	52.0	-0.1	-0.19	
BUTYL	Washing	Methanol	50.6	50.4	-0.2	-0.40	
Neoprene	Washing	Pentane	85.3	85.4	+0.1	+0.12	
Neoprene	Washing	Pentane	85.6	85.5	-0.1	-0.12	0.0
Neoprene	Washing	Pentane	84.5	84.4	-0.1	-0.12	
Neoprene	Washing	Pentane	85.3	85.4	+0.1	+0.12	

Table 4. Comparison of Precision (95% Confidence Interval CI) and Accuracy of Measurements for a Microbalance (TGA D471 mB) and a Macrobalance (H15 D471 MB) for Two Elastomer Sample Types and Two Liquids. Parentheses Indicate 95% CI Value as a Percentage of Mean Value.

a. Equilibrium Solubility, Corrected for Fraction Extracted

Elastomer/ Solvent*/ Balance	No. Reps	Mean Value EqS %	95 % Confidence Interval EqS
BUTYL/PCE/ TGA D471 mB	4	302.5	10.18 (±3.4%)
Accuracy of EqS relative to H15 D471 MB = <u>+1.85%</u>			
BUTYL/PCE/ H15 D471 MB	4	297.0	10.38 (±3.5%)
BUTYL/CEESS/ TGA D471 mB	3	41.2	1.31 (±3.2%)
Accuracy of EqS relative to H15 D471 MB = <u>+1.23%</u>			
BUTYL/CEESS/ H15 D471 MB	3	40.7	0.74 (±1.7%)
Neoprene/PCE/ TGA D471 mB	4	223.6	5.14 (±2.3%)
Accuracy of EqS relative to H15 D471 MB = <u>+2.76%</u>			
Neoprene/PCE/ H15 D471 MB	4	217.6	7.64 (±3.5%)

* Boiling Points: PCE, 121 °C; CEESS, 208 °C

Table 4. Comparison of Precision (95% Confidence Interval CI) and Accuracy of Measurements for a Microbalance (TGA D471 mB) and a Macrobalance (H15 D471 MB) for Two Elastomer Sample Types and Two Liquids. Parentheses Indicate 95% CI Value as a Percentage of Mean Value. (Continued)

b. Diffusion Coefficient

Elastomer/ Solvent*/ Balance	No. Reps	Mean Value DC cm ² /sec	95 % Confidence Interval DC
BUTYL/PCE/ TGA D471 mB	4	9.63E-08	0.67 (±7.0%)
Accuracy of EqS relative to H15 D471 MB = <u>+1.85%</u>			
BUTYL/PCE/ H15 D471 MB	4	NA	NA
BUTYL/CEESS/ TGA D471 mB	3	1.25E-08	0.03 (±2.0%)
Accuracy of EqS relative to H15 D471 MB = <u>+1.23%</u>			
BUTYL/CEESS/ H15 D471 MB	3	NA	NA
Neoprene/PCE/ TGA D471 mB	4	14.6E-08	2.37 (±16.2%)
Accuracy of EqS relative to H15 D471 MB = <u>+2.76%</u>			
Neoprene/PCE/ H15 D471 MB	4	NA	NA
* Boiling Points: PCE, 121 °C; CEES, 208 °C			

Table 4. Comparison of Precision (95% Confidence Interval CI) and Accuracy of Measurements for a Microbalance (TGA D471 mB) and a Macrobalance (H15 D471 MB) for Two Elastomer Sample Types and Two Liquids. Parentheses Indicate 95% CI Value as a Percentage of Mean Value. (Continued)

c. Fraction Extracted

Elastomer/ Solvent*/ Balance	No. Reps	Mean Value Ext %	95 % Confidence Interval Ext
BUTYL/PCE/ TGA D471 mB	4	7.7	2.86 (±37%)
Accuracy of EqS relative to H15 D471 MB = <u>+1.85%</u>			
BUTYL/PCE/ H15 D471 MB	4	8.8	1.02 (±12%)
BUTYL/CEESS/ TGA D471 mB	3	2.9	0.91 (±31%)
Accuracy of EqS relative to H15 D471 MB = <u>+1.23%</u>			
BUTYL/CEESS/ H15 D471 MB	3	2.6	0.96 (±36%)
Neoprene/PCE/ TGA D471 mB	4	16.8	0.72 (±4%)
Accuracy of EqS relative to H15 D471 MB = <u>+2.76%</u>			
Neoprene/PCE/ H15 D471 MB	4	16.2	0.56 (±3%)

* Boiling Points: PCE, 121 °C; CEESS, 208 °C

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